

REMARKS

The specification has been amended. A substitute specification (clean and marked copies) are attached to this response. No new matter has been added.

Claims 1-14 have been canceled, and new claims 15-24 added. New claim 15 corresponds to canceled claims 1/2, new claim 17 corresponds to canceled claims 1/4, and new claim 19 corresponds to canceled claims 1/6.

Claims 1, 13 and 14 have been rejected under 35 USC 102(b) as anticipated by Kato. The rejection is respectfully traversed. The rejections is moot since claim 15 (incorporating canceled claims 1 and 2) are allowed by the Examiner. Claims 23 and 24 (corresponding to canceled claims 13 and 14) depend from allowable claim 15, and are therefore similarly patentable.

Claims 6, 7, 8 and 10-12 have been rejected under 35 USC 103(a) as unpatentable over Kato in view of Oshima and/or Kojima. The rejection to claims 10-12 is moot due to their cancellation. Claim 19 corresponds to canceled claims 1/6, as noted above, and claims 20-22 correspond to canceled claims 7-9, respectively. Claim 22 (canceled claim 9) has not been rejected in the Office Action. Applicants therefore proceed with the understanding that this claim would be allowable if rewritten in independent form to include any base and intervening claims.

Kato discloses a gas sensor which comprises a main pumping cell pumping oxygen in a first chamber, and a feedback control system comparing a partial pressure of oxygen in the first chamber, with a first reference value to control the main pumping cell such that the partial pressure of oxygen has a predetermined value at which NO is not decomposed. The gas sensor further comprises an auxiliary pumping cell, which pumps oxygen in a second chamber, and a measurement pumping cell, which pumps oxygen generated by decomposition of NOx. Moreover, a correcting control system for correction and control of the feedback control system as a function of a difference between the second reference value and a value of a pumping current flowing through the auxiliary pumping cell is provided to obtain a constant oxygen concentration in the second chamber. A self-diagnosis unit serves to compare the pumping current with a predetermined range and to determine, on the basis of the results of comparison, whether a malfunction is present or not.

In particular, with reference to Fig. 8, a sensor comprises a main pumping cell 28 including an outer electrode 26 on a solid electrolyte layer 12f and an inner pumping electrode 24 adjoining a first chamber 20. A measurement pumping cell 58 is formed by a detecting or measuring electrode 172 arranged at a second chamber 22 on the solid electrolyte layer 12d and by the outer electrode 26 (see, column 17, lines 41 to 50). A measuring cell 170 for measuring the oxygen partial pressure relative to a reference value is formed by the measuring electrode 172 and a reference electrode 32 at a reference gas chamber 14. A pumping current I_{p2} between the measuring electrode 172 and the outer electrode 26 is controlled by a current source 60A as a function of the Nernst potential of the measuring electrode 172 measured by the voltmeter 174 (cf. Kato, column 17, line 2). The pumping current I_{p2} is detected by an ammeter 62 (see, column 10, lines 3 to 12 and 23 to 25; and column 17, lines 41 to 50).

In the claimed invention (e.g. claim 19), on the other hand, the measuring electrode is checked by setting a predetermined oxygen concentration in the measurement cavity, impressing a pumping current between the measuring electrode and external electrode that is set such that a predetermined value of the Nernst potential is present at the measuring electrode, varying the oxygen concentration in the measurement cavity and adjusting the pumping current between the measuring electrode and external electrode such that the Nernst potential at the measuring electrode is kept constant, determining the proportionality factor between the pumping current and oxygen concentration, comparing the determined proportionality factor with a reference value, and establishing a defect in the measuring electrode when the determined proportionality factor deviates from the reference value by more than a predetermined amount. Thus, the oxygen concentration is varied and it is detected when the Nernst potential jumps or how great the proportionality factor between the pumping current and the oxygen concentration is.

Accordingly, the claimed invention comprises detection of the size of the oxygen ion current via or by the measuring electrode via the pumping current from the measuring electrode to the external electrode, so that the function or the state of the measuring electrode can be checked. This is not possible in the applied references. Rather, Kato provides an auxiliary pumping cell 52 which comprises the auxiliary pumping electrode adjoining the second chamber 22, a variable source of current 54A controlled by a voltage V_1 , and the outer electrode 26. An auxiliary measuring cell 202 for measuring the oxygen partial pressure in the second chamber 22

comprises the auxiliary pumping electrode 50, separated therefrom by the solid electrolyte layer 12d, the reference electrode 32, as well as the voltage sensor 206 which senses the voltage V_{p1} used to control the source of current 54A (see, column 17, lines 51 to 63). The current I_{p1} of the auxiliary pumping cell 52 is supplied to the self-diagnosis unit 100. Hence, although the measuring cells 170 and 172 and the auxiliary cells 52 and 202 have the outer electrode 26 and the reference electrode 32 in common and adjoin the second chamber 22, they are completely independent of one another. Thus, in particular, the pumping current I_{p2} from the measuring electrode 172 to the external electrode 26 is not used for self-diagnosis.

Since the auxiliary pumping electrode 50 and the measuring electrode 172 are spatially separated from one another, the auxiliary cells cannot establish a defect in the measuring electrode 172 either, because the oxygen flows pass only over the auxiliary pumping electrode 152 and not over the measuring electrode 172. In Kato, for example, the self-diagnosis is performed via the auxiliary cells therein, and not via the measuring electrodes. Kato does not give the person skilled in the art any hint or motivation to use the measuring cells instead of the auxiliary cells for self-diagnosis. Hence, even a combination of Kato in view of Oshima is irrelevant.

Simply stated, a person skilled in the art would not have been motivated to combine the self-diagnosis to the measuring cell. In contrast thereto, the invention provides for the detection of a jump in the Nernst potential or for the determination of a proportionality factor between the pumping current and the oxygen concentration. While Kato discloses a method for the self-diagnosis of an NO_x sensor wherein a lambda signal characterizing the lambda value of the waste gas is determined, the determined values of the lambda signal are compared with lambda values of the waste gas that are plausible for predetermined parameters of operation, and an NO_x sensor diagnosis signal is formed depending on the result of said comparison.

Since the recited method is not disclosed by the applied prior art, either alone or in combination, claim 19 is allowable. Claims 20 and 21, depending from claim 19, are similarly patentable.

In view of the above, Applicants submit that this application is in condition for allowance. An indication of the same is solicited. The Commissioner is hereby authorized to

**METHOD FOR OPERATING A MEASURING PROBE FOR MEASURING A
GAS CONCENTRATION**

CLAIM FOR PRIORITY

[0001] This application claims the benefit of priority to DE 10312732.1, filed March 21, 2003, the contents of which are hereby incorporated by reference.

TECHNICAL FIELD OF THE INVENTION

[00010002] The invention relates to a method for operating a measurement probe for measuring a gas concentration in a measuring gas with the aid of a solid electrolyte which conducts oxygen ions and has a measurement cavity for holding the measuring gas, a measuring electrode and an external electrode, a pumping current flowing between the measuring electrode and external electrode transporting oxygen ions from the measuring electrode to the external electrode.

BACKGROUND OF THE INVENTION

[00020003] It is known for the purpose of measuring the NOx concentration in a measuring gas, for example the exhaust gas of an internal combustion engine, to use a sensor such as is described, for example, in the publication DE 199 07 947 A1. The mode of operation of the sensor is based on the Nernst principle. At temperatures above 350.degree. C., the solid electrolyte material of the sensor is simultaneously a very good oxygen ion conductor and a poor ion conductor with reference to other chemical elements.

[00030004] Different oxygen concentrations on the two sides of the solid electrolyte lead to different electric potentials of the electrodes arranged on the respective sides. The potential difference then constitutes a measure of the difference in the oxygen concentration on the two sides of the solid electrolyte.

[00040005] The quantity of remaining oxygen in the exhaust gas fluctuates strongly with a change in the air/fuel ratio, the lambda value. If the air/fuel mixture is in the so-called

rich range (lambda value<1), in which the fuel is present in stoichiometric excess, the result is typically a Nernst voltage between the two electrodes of 800 to 1000 mV. For the so-called lean mixtures (lambda value>1), where the oxygen predominates over the air, the result is a Nernst voltage down to approximately 100 mV. Upon transition from rich to lean mixture, the Nernst voltage therefore changes discontinuously in the region about the stoichiometric lambda value 1 by 700 to 800 mV.

[00050006] The measuring sensor in the abovenamed DE 199 07 947 A1 has two measuring cells in a body made from an oxygen-conducting solid electrolyte. Oxygen is pumped out of the first measuring cell, which is fed the measuring gas via a diffusion barrier, by means of a first pumping current, and a first oxygen concentration is set thereby.

[00060007] The measuring gas diffuses from the first measuring cell into the second measuring cell via a diffusion barrier. The oxygen content is further lowered in the second measuring cell by means of a second pumping current, and an oxygen concentration is set. NOx is decomposed at a measuring electrode arranged in the second measuring cell, and the oxygen thereby formed is pumped off by means of a third pumping current. The third pumping current then constitutes a measure of the NOx concentration in the measuring gas.

[00070008] In order to set the pumping current, the Nernst potential at the electrodes is tapped in the respective measuring cells, said potential being determined relative to the oxygen content of a reference gas to which a reference electrode is exposed.

[00080009] Depending on the tendency to oxidation of the electrode material as a consequence of controller deficiencies or manufacturing fluctuations and/or material tolerances, it can happen that the electrode material oxidizes more or less strongly and changes its volume owing to the incorporation of oxygen. The corruption of the measurement signal associated therewith can have the effect that the emission values

prescribed for motor vehicles can no longer be met using a sensor changed in this way.

SUMMARY OF THE INVENTION

[00090010] ~~This is the starting point of the invention, which is based on the object of~~
~~The invention relates to~~ developing a generic method such that the reliability of the measured value determined by the measurement probe is increased.

[00100011] ~~This object is achieved according to the invention by virtue of the fact that in~~
~~a method of the type mentioned at the beginning~~In the invention, the integrity of the measuring electrode is checked by determining the electrode area effectively available for oxygen diffusion.

[00110012] ~~The invention is based on the idea that~~In one embodiment of the invention, the corrupted measured values stem from a detachment of the electrode material and/or a cover layer lying thereover, owing to mechanical stresses or the tendency of the material to oxidize. The detachment is detected according to the invention by determining the electrode area effectively available for the oxygen diffusion. A range of preferred methods are specified below for this determination.

[00120013] ~~In a first preferred refinement~~another embodiment of the method according to the invention, the measuring electrode is checked by setting a predetermined oxygen concentration in the measurement cavity, impressing a predetermined constant pumping current between the measuring electrode and external electrode, measuring the resulting Nernst potential at the measuring electrode, measuring the period of time until the measured Nernst potential jumps from small to large values, comparing the measured period of time with a predetermined threshold value, and detecting a defect in the measuring electrode when the measured period of time falls below the predetermined threshold value.

[00130014] It is expedient in this case to select the predetermined constant pumping

current to be so large that even in the case of an intact measuring electrode more oxygen is transported from the measuring electrode to the external electrode than can subsequently diffuse into the measuring electrode.

[00140015] According to another ~~preferred refinement~~embodiment of the method according to the invention, the measuring electrode is checked by impressing a predetermined constant pumping current between the measuring electrode and external electrode, varying the oxygen concentration in the measurement cavity and measuring the resulting Nernst potential at the measuring electrode, determining the oxygen concentration at which the measured Nernst potential jumps between small and large values, comparing the determined oxygen concentration with a reference value, and detecting a defect in the measuring electrode when the determined oxygen concentration deviates from the reference value by more than a predetermined amount.

[00150016] The oxygen concentration in the measurement cavity is advantageously determined by measuring the Nernst potential at an auxiliary electrode in the measurement cavity.

[00160017] In accordance with a further ~~advantageous variant~~embodiment of the method according to the invention, the measuring electrode is checked by setting a predetermined oxygen concentration in the measurement cavity, impressing a pumping current between the measuring electrode and external electrode that is set such that a predetermined value of the Nernst potential is present at the measuring electrode, varying the oxygen concentration in the measurement cavity and adjusting the pumping current between the measuring electrode and external electrode such that the Nernst potential at the measuring electrode is kept constant, determining the proportionality factor between the pumping current and oxygen concentration, comparing the determined proportionality factor with a reference value, and detecting a defect in the measuring electrode when the determined proportionality factor deviates from the reference value by more than a predetermined amount.

[00170018] It is preferred when carrying out the method to set two predetermined values of the oxygen concentration in the measurement cavity at which the pumping current is set in each case such that the predetermined value of the Nernst potential is present at the measuring electrode, and the proportionality factor between the pumping current and oxygen concentration is determined from the two values for the pumping current set. Since there is a linear relationship between pumping current and oxygen concentration, two measured values suffice for determining the proportionality factor.

[00180019] The detachment of a cover layer lying over the measuring electrode is advantageously detected from the fact that the determined proportionality factor exceeds a reference value by more than a predetermined amount. By contrast, the detachment of the cover layer from the measuring electrode generally obtains when the determined proportionality factor falls below the reference value by more than a predetermined amount.

[00190020] According to yet a further ~~advantageous variantembodiment~~ of the method according to the invention, the measuring electrode is checked by setting a predetermined oxygen concentration in the measurement cavity, impressing a pumping current between the measuring electrode and external electrode that is set such that a predetermined value of the Nernst potential is present at the measuring electrode, comparing the pumping current set with a reference value, and detecting a defect in the measuring electrode when the pumping current set deviates from the reference value by more than a predetermined amount.

[00200021] In this variantembodiment, a detachment only of the cover layer of the measuring electrode is detected when the pumping current set exceeds the reference value by more than a predetermined amount. The detachment of cover layer and measuring electrode is seen in the fact that the pumping current set falls below the reference value by more than a predetermined amount.

[00210022] The integrity of the measuring electrode can advantageously be checked with

each start of the measurement probe. Alternatively, or in addition, the measuring electrode can be checked on demand, in particular by a control unit.

BRIEF DESCRIPTION OF THE DRAWINGS

[00220023] The invention is explained in yet further detail below by way of example with reference to the drawings, in which:

[00230024] FIG. 1 shows a schematic sectional illustration of an NOx sensor with associated circuitry, and,

[00240025] FIG. 2 shows a flowchart for carrying out an operating method according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

[00250026] FIG. 1 shows a schematic sectional illustration of an NOx sensor 10 for detecting the NOx concentration in the exhaust duct of an internal combustion engine. The NOx sensor 10 is constructed from a solid electrolyte, in the exemplary embodiment from ZrO₂. The exhaust gas to be measured diffuses into a first measuring cell 14 via a diffusion barrier 12.

[00260027] The oxygen content of the first measuring cell 14 is measured in a known way by tapping a Nernst voltage V_0 between a first electrode 16 in the measuring cell 14 and a reference electrode 20 arranged in the reference cell 18. The oxygen content in the first measuring cell 14 is therefore referred to the oxygen content in the reference cell 18.

[00270028] On the basis of the measured oxygen content in the first measuring cell 14, the voltage-controlled current source U_0 is used to adjust, by a first pumping current I_{p0} , a predetermined oxygen concentration in the first measuring cell 14 in the range of a few ppm.

[00280029] The measuring gas diffuses from the first measuring cell 14 into a second measuring cell 24 via a second diffusion barrier 22. In the second measuring cell 24, a second voltage-controlled current source U1 lowers the oxygen content of the measuring gas to values in the range of a few 10.⁻³ ppm by means of a second Nernst voltage V1 between a second electrode 26 and the reference electrode 20. For this purpose, the current source U1 drives a second pumping current Ip1 between the second electrode 26 and an external electrode 28.

[00290030] NOx is now catalytically decomposed at a measuring electrode 30 in the second measuring cell 24, and the oxygen produced is transported to the external electrode 28 from the measuring electrode 30 via a third pumping current Ip2. The oxygen content in the second measuring cell 24 is lowered by the second pumping current Ip1 so far that the third pumping current Ip2 is substantially borne only by the oxygen ions that originate from the decomposition of NOx at the measuring electrode 30. The third pumping current Ip2 is therefore a measure of the NOx concentration in the second measuring cell 24, and thus also in the exhaust gas to be measured.

[00300031] FIG. 2 shows a flowchart for carrying out an operating method according to the invention, in which the integrity of the measuring electrode 30 is checked, for example on demand by a control unit.

[00310032] For this purpose, after a step S10, in which the method is started, there is firstly set in a step S12 in the second measuring cell 24 a predetermined oxygen concentration that is also set in the measuring electrode 30 with a third pumping current Ip2 switched off for the time being. The oxygen concentration is selected to be so high, 2500 ppm in the exemplary embodiment, that it is possible to neglect an NOx concentration that may be present, for example 500 ppm, by comparison therewith as regards the content of oxygen atoms.

[00320033] A predetermined constant pumping current Ip2=I0 between the measuring

electrode 30 and external electrode 28 is then driven at an instant $t0=0$ in a step S14, and the resulting Nernst potential $V2$ at the measuring electrode 30 is measured in step S16. The incipient pumping activity removes oxygen from the electrode 30, it also being possible for oxygen to diffuse subsequently into the measuring electrode 30 from the gas space via a cover layer of the measuring electrode 30 through the diffusion-limiting cover layer.

[00330034] It is now checked in a step S18 whether the measured Nernst potential $V2$ jumps from small to large values, and the period of time $t0$ up to this jump is determined in step S20. The period of time $t0$ thus determined is then compared in a step S22 with a predetermined threshold value t_thres . In the event of a reduced effective boundary layer owing to electrode detachment, that is to say of a diminished gas phase/electrode-material/solid electrolyte interface, the volume of the measuring electrode 30 is also reduced together with the contact surface to the electrolyte material. Consequently, the oxygen quantity is also smaller inside the measuring electrode 30 and can be pumped out more quickly by means of a constant pumping current $Ip2$ than in the case of a larger electrode area.

[00340035] It goes without saying that the pumping current $Ip2$ is selected to be so large that even in the case of an intact measuring electrode it is possible for more oxygen to be removed than can subsequently diffuse.

[00350036] The oxygen quantity inside the measuring electrode 30 requires a defined charge quantity during transport as oxygen ions through the solid electrolyte that corresponds to the integral over $Ip2*dt$, that is to say to the value $I0*t0$, given a constant current. A complete removal of the oxygen from the measuring electrode 30 is detected via the Nernst potential $V2$, which then jumps suddenly from small values, approximately 100 mV in the exemplary embodiment, to large values, approximately 800 to 1000 mV in the exemplary embodiment. If, because of an electrode detachment, the electrode area is now reduced, the measuring electrode thus no longer being intact, $t0$ will lie, given a constant pumping current $I0$, below a predetermined threshold value t_thres that was

determined previously as limiting value for the detection of a defective electrode.

[00360037] Consequently, a defect in the measuring electrode is detected in a step S24 when the measured period of time t_0 falls below the predetermined threshold value t_{thres} . Otherwise, the electrode is evaluated as intact in step S26.

[00370038] According to another exemplary embodiment of the operating method, instead of the approach of switching on the second pumping current I_{p2} at a specific time instant and determining the period of time until the jump in the Nernst potential, the oxygen concentration is now varied in the second measuring cell 24 given a constant pumping current I_{p2} . If the oxygen concentration is now tuned, I_{p2} therefore follows the external oxygen concentration. Since the quantity of oxygen that can subsequently diffuse in the event of a reduced effective surface of the measuring electrode is smaller than given an intact electrode, the Nernst potential V_2 already jumps at a higher oxygen concentration than in the case of an intact electrode. The oxygen concentration in the second measuring cell 24 is measured in the exemplary embodiment via the Nernst potential V_1 of the second electrode 26, and so in the event of a defective electrode 30 the jumping point of the Nernst potential V_2 is at a value of the Nernst potential V_1 differing from the reference value. It goes without saying that a defect is not diagnosed until an established permitted deviation from the reference value is exceeded.

[00380039] In a further exemplary embodiment of the operating method according to the invention, the oxygen concentration in the second measuring cell 24 is set to a predetermined value, while the pumping current I_{p2} is controlled such that a predetermined value of the Nernst potential is present at the measuring electrode 30. If the oxygen concentration in the second measuring cell 24 is now tuned and I_{p2} is adjusted in the process such that the Nernst potential remains constant at the measuring electrode, I_{p2} then follows the external oxygen concentration. Since the quantity of oxygen that can subsequently diffuse given a reduced effective surface of the measuring electrode is smaller than given an intact electrode, in the case of a reduced electrode surface a smaller proportionality factor of I_{p2} in relation to the oxygen concentration is

set up in the second measuring cell 24 than for the intact measuring electrode 30.

[00390040] Two measuring points suffice for determining the proportionality factor because of the linear relationship between the pumping current I_{p2} and oxygen concentration. If only the cover layer of the measuring electrode is detached owing to a crack, a substantially larger proportionality factor (approximately twice as large in the exemplary embodiment) than for an intact electrode results, in a fashion largely independent of the size of the crack. If, by contrast, the cover layer and measuring electrode are detached jointly, a smaller proportionality factor, and an offset in the current/concentration relationship that is caused by the brittle cover layer is seen because of the smaller area of the measuring electrode 30.

[00400041] The integrity of the measuring electrode 30 can also be determined with the aid of a measurement given only a single oxygen concentration. For this purpose, an increased oxygen concentration, 500 ppm to 750 ppm in the exemplary embodiment, is set and the pumping current I_{p2} required to reach a predetermined Nernst potential is measured. A mean value that serves as reference value results in the case of intact electrode 30. Detachment of only the cover layer results in a higher current value, while detachment of the cover layer and measuring electrode results in a lower current value. For example, if the reference value is exceeded by 30% or more, a detachment only of the cover layer is detected, and if the reference value has fallen below by 30% or more, detachment of the cover layer and measuring electrode is detected.